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(54) A CONDUCTIVE RESIN SHEET AND A METHOD OF ITS PRODUCTION

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(57) Abstract

Purpose: The purpose of this invention is to present a method of producing a semiconductive resin sheet made from a polymer blend of polyimide and (un)doped polyaniline with stable conductivity, even with changes in the environment.

Structure: The preferred method of producing a semiconductive resin sheet of this invention involves casting onto a substrate a film-forming solution, which comprises polyamide acid, undoped polyaniline, and a dopant that can dope undoped polyaniline to conductivity, to form a layer of the aforementioned solution on the substrate, heating the product to 60 to 200°C to form a resin sheet on the substrate, peeling the resin sheet from the substrate, and then heating this resin sheet to 250 to 400°C for imidation of the polyamide acid.

Scope of the Patent Claim

[Claim 1] A semiconductive resin sheet, which is made from a polymer blend of

polyimide and undoped polyaniline, has a modulus of 200 kgf/mm² or higher, and has volume resistivity of 10⁷ to 10¹⁴ Ω·cm.

[Claim 2] A method of producing a conductive resin sheet, where a film-forming solution comprising polyamide and undoped polyaniline is cast onto a substrate to form a layer of the aforementioned film-forming solution on the substrate, the product is heated to a temperature of 60 to 200°C to form a resin sheet on the substrate, then this resin sheet is peeled from the substrate, and the resin sheet is heated to 250 to 400°C for imidation of the polyamide acid. The conductive resin sheet that is obtained has a modulus of 200 kgf/mm² or higher and a volume resistivity of 10⁷ to 10¹⁴ Ω·cm.

[Claim 3] A method of producing a semiconductive resin sheet, which is characterized by the fact that a film-forming solution, which comprises polyamide acid, polyaniline, and dopant that is capable of doping this polyaniline to conductivity, is cast on a substrate to form a layer of the aforementioned film-forming solution on the substrate, the product is heated to a temperature of 60 to 200°C to form a resin sheet on the substrate, the resin sheet is peeled from the substrate, and then this resin sheet is heated to a temperature of 250 to 400°C for imidation of the polyamide.

Detailed Explanation of the Invention

[0001]

Industrial Field of Use

This invention pertains to a method of producing a conductive resin sheet of superior semi-conductivity, toughness, and mechanical strength from a polymer blend comprising polyimide and undoped or doped polyaniline. This type of semiconductive resin sheet is ideal for electrode materials of cells, magnetic shields, electrostatic absorption films, anti-static materials, video recorder parts, electronic devices, etc.

[0002]

Prior Art

It is a known fact that polyimide can be made conductive by adding a conductive filler, such as carbon, carbon fibers, graphite, metal particles, metal oxide particles, etc., to polyimide. Nevertheless, when these type of conductive fillers are added to polyimide and the polyimide is made into a sheet that is conductive, the sheet that is obtained has poor mechanical properties, and when the sheet is finished or used, it cannot withstand tension and breaks. Moreover, polyimide sheets obtained by this type of method do not have uniform or reproducible surface resistivity.

[0003]

On the other hand, semiconductive polymer blends made from conductive polyaniline and other resins have been presented in, for instance, Japanese Kokai Patent No. Hei 4(1982)-63865. This type of semiconductive polymer blend is obtained by preparing a mixture of undoped polyaniline, that is polyaniline that has not been doped with a dopant, and another resin and then performing doping treatment on this blend with a dopant. However, the dopants can be easily removed by moisture or heat and therefore, there is a problem in that electrical resistance readily changes with the environment. Furthermore, there is also a problem in that many

processes, including film forming, doping, washing, and drying, are needed to obtain a conductive polymer blend by the aforementioned method.

[0004]

Problems to be Solved by the Invention

This invention solves the aforementioned problems with conventional semiconductive resin sheets, its purpose being to present a semiconductive resin sheet with stable semi-conductivity, even with changes in the environment, and a method for producing this sheet.

[0005]

Means for Solving Problems

The semiconductive resin sheet of this invention comprises a polymer blend of polyimide and undoped polyaniline and it has a modulus of 200 kgf/mm² or higher and a volume resistivity of 10^7 to 10^{14} Ω cm.

[0006]

By means of this invention, this type of semiconductive resin sheet can be obtained by casting onto a substrate a film-forming solution containing polyamide acid and undoped polyaniline in order to form a layer of the aforementioned film-forming solution on the substrate, heating this product to a temperature of 60 to 200°C to form a resin sheet on the substrate, peeling the resin sheet from the substrate, and then heating this resin sheet to a temperature of 250 to 400°C for imidation of the polyamide acid.

[0007]

This invention further presents a method of producing a semiconductive resin sheet of higher conductivity comprising polyimide and doped polyaniline, that is polyaniline that has

been doped with dopant. This semiconductive resin sheet can be obtained by this invention by casting a film-forming solution containing polyamide acid, polyaniline and dopant that can dope this polyaniline to conductivity on a substrate to form a layer of the aforementioned film-forming solution on the substrate, heating the product to a temperature of 60 to 200°C to form a resin sheet on the substrate, and then peeling the resin sheet from the substrate and then heating the resin sheet to a temperature of 250 to 400°C for imidation of the polyamide acid.

[0008]

It is preferred that the doped or undoped polyaniline account for 1 to 90 wt% of the semiconductive resin sheet made from the aforementioned polymer blend of this invention.

[0009]

The term semiconductive resin sheet in this invention refers to a resin sheet whose volume resistivity is within a range of 10^7 to 10^{15} $\Omega\cdot\text{cm}$.

[0010]

The polyamide acid can be obtained in solution form by dissolving an almost equimolar mixture of a tetracarboxylic dianhydride or its derivative and its diamine in an organic solvent and reacting the mixture in solution form. Consequently, the polyamide acid is prepared as a precursor of the polyimide and then this polyamide acid is heated to form the insoluble, infusible polyimide.

[0011]

It is preferred that by means of this invention, the polyamide acid be an acid that is obtained by reacting an aromatic tetracarboxylic dianhydride in an aromatic diamine.

[0012]

As previously explained, by means of this invention, a polyamide acid solution is prepared while a solution comprising undoped polyaniline, or a solution comprising undoped polyaniline and a dopant that can dope this polyaniline to conductivity is separately prepared. These solutions are then mixed to obtain the film-forming solution. This film-forming solution is cast onto an appropriate substrate, such as the surface of a sheet of glass, metal, resin, etc., or the outer surface or inner surface of a tube made from glass, metal, resin, etc. The product is then dried; and heated for imidation of the polyamide acid to obtain a semiconductive resin sheet made from a polymer blend of polyimide and polyaniline. When the aforementioned tube substrate is used, a tube-shaped product can be obtained, and this type or tube-shaped product is also included in the description of sheet products of this invention.

[0013]

Examples of the aforementioned aromatic tetracarboxylic dianhydride used to prepare the polyamide acid are pyromellitic dianhydride, 3,3',4,4'- benzophenone tetracarboxylic dianhydride, 3,3',4,4'- biphenyl tetracarboxylic dianhydride, 2,3,3',4'- biphenyl tetracarboxylic dianhydride, 2,3,6,7-naphthalene tetracarboxylic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 1,4,5,8- naphthalene tetracarboxylic dianhydride, 2,2,'-bis(3,4-dicarboxyphenyl) propane dianhydride, bis (3,4-dicarboxyphenyl) sulfone dianhydride, etc. These can be used alone or several can be used together.

[0014]

Examples of the aforementioned aromatic diamine are 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl methane, 3,3'-diamino diphenyl methane, p-phenylene diamine, m-phenylene diamine, benzidine, 3,3'-dimethoxy benzidine, 4,4'-diamino diphenylsulfone, 4,4'-diamino diphenylsulfide, 4,4'-diamino diphenylpropane, 2,2-bis [4-(4-aminophenoxy) phenyl] propane,

etc. These also can be used alone, or several can be used together.

[0015]

Moreover, N-methyl-2 pyrrolidone, N,N'-dimethylacetamide, dimethylsulfoxide, hexamethylene phosphoric triamide, etc., can be used as the aforementioned organic polar solvent. When necessary, phenols, such as cresole, phenol, xylenol, etc., hydro-carbons, such as hexane, benzene, and toluene, etc., can be mixed with these organic polar solvents. These solvents also can be used alone or as a mixture of two or more.

[0016]

The aforementioned aromatic tetracarboxylic dianhydride and aromatic diamine are reacted in the aforementioned solvent in solution form. The concentration of the starting materials, consisting of the aforementioned anhydride and diamine, in the organic solvent when a polyamide acid solution is to be obtained is usually within a range of 5 to 30 wt%, preferably 10 to 25 wt%. Although it also depends on the anhydride and the diamine that are used, polyamide acid can usually be obtained as a solution by reacting the starting materials for 2 to 10 hours within a temperature range of 80°C or lower, preferably 5 to 50°C.

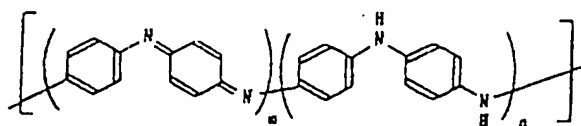
[0017]

When the aromatic tetracarboxylic dianhydride and aromatic diamine are reacted in solution form, viscosity of the solution rises as the reaction proceeds. However, by means of the present invention, a polyamide acid solution whose inherent viscosity as determined using an N-methyl-2-pyrrolidone solution at a temperature of 30°C is 0.5 or higher should be used. Thus, it is possible to obtain sheets with excellent reliability of mechanical strength by using a polyamide acid solution with an inherent viscosity of 0.5 or higher.

[0018]

The polyaniline that is used in the present invention is a polyaniline that is soluble in solvents in an undoped state and has as its main repeating units, phenylene diamine structural units and quinone diamine structural units represented by general formula (I).

[0019]



[Chemical Formula 1]

[0020]

(In the formula, m and n are the molar ratio of the quinone diamine structural units and phenylene diamine structural units comprising the repeating units, respectively, $0 < m < 1$, $0 < n < 1$, and $m + n = 1$.) This type of polyamide is referred to as a quinone diamine-phenylene diamine-type polyaniline. Refer to Japanese Kokai Patent No. Hei 3(1991)-28229 for details on the properties and production of this type of polyaniline.

[0021]

As described in Japanese Kokai Patent No. Hei 3(1991)-28229, the polyaniline that is used in this invention is preferably a polyaniline where, of the skeletal vibrations of the para-substituted benzene in the laser-Raman spectrum obtained by excitation with light having a wavelength of 457.9 nm in an undoped state, the ratio I_a/I_b of intensity I_a of the Raman line for skeletal stretching vibration at a frequency higher than 1600 cm^{-1} and intensity I_b of the Raman line of skeletal stretching vibrations at a frequency lower than 1600 cm^{-1} is at least 1.0.

Furthermore, it is also preferred that the polyaniline used in this invention have a limiting viscosity (η) as determined in N-methyl pyrrolidone at 30°C of 0.40 dl/g or higher. As described in detail in Japanese Kokai Patent Hei 3(1991)-28229, when compared to conventional polyaniline, polyaniline with this laser-Raman spectrum property has a higher molecular weight and can be differentiated by its solvent solubility. Moreover, it can also be structurally differentiated from conventional polyaniline.

[0022]

As previously mentioned, the polyaniline in this invention is quinone diamine/phenylene diamine-type polyaniline that is soluble in organic solvents in an undoped state and has a specific limiting viscosity and the aforementioned laser-Raman spectrum property. Moreover, as described in detail in Japanese Kokai Patent No. Hei 3(1991)-28229, an aqueous solution of an oxidizing agent, whose reference electrode potential is 0.6 V or higher, with this standard reference potential defined as the electromotive force in a reduction half-cell reaction based on a reference hydrogen electrode, is gradually added to aniline in a solvent in the presence of a protic acid, whose acid dissociation constant pK_a is 3.0 or lower, while maintaining a temperature of 5°C or less, preferably 0°C or less. This aqueous solution is added at the molar equivalent, which is defined as the amount that is obtained when 1 mole of oxidizing agent is divided by the number of electrons needed to reduce 1 molecule of oxidizing agent, preferably 2 molar equivalents or higher, particularly 2 to 2.5 molar equivalents, to 1 mole aniline. As a result, oxidation polymer of aniline that has been doped with the aforementioned protic acid (referred to

below as doped polyaniline) is generated. Next, the doped polyaniline is undoped by a basic substance.

[0023]

Thus, oxidation polymerization of aniline is performed in the presence of a protic acid to obtain polyaniline. Next, this polyaniline is undoped. The polyaniline that is obtained as a result has a high molecular weight and is soluble in a variety of organic solvents. Examples of such organic solvents include N-methyl-2-pyrrolidone, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, 1,3-dimethyl-2-imidazolidinone, sulfolane, etc. Solubility of the polyaniline in this undoped state depends on the average molecular weight of the polyaniline and the solvent, but 0.5 to 100% polymer is dissolved to obtain a solution of 1 to 30 wt%.

[0024]

As previously mentioned, by means of this invention, a semiconductive resin sheet can be obtained from a polymer blend of polyimide and (un)doped conductive polyaniline by preparing a film-forming solution comprising polyamide acid and undoped polyaniline (and dopant that can dope this polyaniline to conductivity), casting this film-forming solution on an appropriate substrate, such as a glass sheet, to form a layer of the film-forming solution on the substrate, heating this product to a temperature of 60 to 200°C to form a resin sheet on the substrate, peeling the resin sheet from the substrate, and then heating this resin sheet to a temperature of 250 to 400°C for imidation of the polyamide acid.

[0025]

A protic acid should be used as the dopant for conductivity when the polyaniline is

doped. Protic acids that are preferred as the dopants are protic acids with an acid dissociation constant pK_a of 4.8 or lower. Examples of such acids include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, hydrofluoroboric acid, hydrofluoro-phosphoric acid, hydrochloric acid, etc., as well as organic acids with an acid dissociation constant pK_a of 4.8 or lower.

[0026]

The organic acid that is used in this invention is, for instance, and organic carboxylic acid or a phenol. It should have an acid dissociation constant pK_a of 4.8 or lower. Such organic acids include aliphatic acids, aromatic acids, araliphatic acids, alicyclic acids, and polybasic acids. These organic acids can also have hydroxyl groups, halogens, nitrile groups, cyano groups, amino groups, etc. Consequently, actual examples of such acids are acetic acid, n-butyric acid, pentadecafluorooctanoic acid, pentafluoro-acetic acid, trifluoroacetic acid, trichloroacetic acid, dichloroacetic acid, monofluoroacetic acid, monobromoacetic acid, monochloroacetic acid, cyanoacetic acid, acetyl acetic acid, nitroacetic acid, triphenyl acetic acid, formic acid, oxalic acid, benzoic acid, m-bromo-benzoic acid, p-chlorobenzoic acid, m-chlorobenzoic acid, p-chlorobenzoic acid, o-nitrobenzoic acid, 2,4-dinitrobenzoic acid, 3,5-dinitrobenzoic acid, picric acid, o-chlorobenzoic acid, p-nitrobenzoic acid, m-nitrobenzoic acid, trimethyl benzoic acid, p-cyanobenzoic acid, m-cyanobenzoic acid, thymol blue, salicylic acid, 5-amino salicylic acid, o-methoxy benzoic acid, 1,6-dinitro-4-chlorophenol, 2,6-dinitrophenol, 2,4-dinitrophenol, p-oxybenzoic acid, bromophenol blue, mandelic acid, phthalic acid, isophthalic acid, maleic acid, fumaric acid, malonic acid, tartaric acid, citric acid, lactic acid, succinic acid, α -alanine, β -alanine, glycine, glycolic acid, thioglycolic acid, ethylene diamine-N,N'-diacetic acid, ethylene diamine N,N,N',N'-tetracetic acid, etc.

Please submit nominations for SOC membership as soon as possible to Jay Vroom, jvroom@croplifeamerica.org. I anticipate making new SOC appointment by early April.

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[0027]

Moreover, the organic acid can have sulfonic acid or sulfuric acid groups. Examples of such organic acids are amino naphthol sulfonic acid, metanilic acid, sulfanilic acid, allyl sulfonic acid, lauryl sulfuric acid, xylene sulfonic acid, chlorobenzene sulfonic acid, methane sulfonic acid, ethane sulfonic acid, 1-propane sulfonic acid, 1-butane sulfonic acid, 1-hexane sulfonic acid, 1-heptane sulfonic acid, , 1-octane sulfonic acid, 1-nonane sulfonic acid, 1-decane sulfonic acid, 1-dodecane sulfonic acid, benzenesulfonic acid, styrene sulfonic acid, p-toluene sulfonic acid, naphthalene sulfonic acid, ethyl benzenesulfonic acid, propyl benzenesulfonic acid, butyl benzenesulfonic acid, pentyl benzenesulfonic acid, hexyl benzenesulfonic acid, heptyl benzenesulfonic acid, octyl benzenesulfonic acid, nonyl benzenesulfonic acid, decyl benzenesulfonic acid, undecyl benzenesulfonic acid, dodecyl benzenesulfonic acid, pentadecyl sulfonic acid, octadecyl benzenesulfonic acid, diethyl benzenesulfonic acid, dipropyl benzenesulfonic acid, dibutyl benzenesulfonic acid, methyl naphthalene sulfonic acid, ethyl naphthalene sulfonic acid, propyl naphthalene sulfonic acid, butyl naphthalene sulfonic acid, phenyl naphthalene sulfonic acid, hexyl naphthalene sulfonic acid, heptyl naphthalene sulfonic acid, octyl naphthalene sulfonic acid, nonyl naphthalene sulfonic acid, pentadecyl naphthalene sulfonic acid, octydecyl naphthalene sulfonic acid, dimethyl naphthalene sulfonic acid, diethyl naphthalene sulfonic acid, dipropyl naphthalene sulfonic acid, dibutyl naphthalene sulfonic acid, dipentyl naphthalene sulfonic acid, dihexyl naphthalene sulfonic acid, diheptyl naphthalene sulfonic acid, dioctyl naphthalene sulfonic acid, dinonyl naphthalene sulfonic acid, trimethyl naphthalene sulfonic acid, triethyl naphthalene sulfonic acid, tripropyl naphthalene sulfonic acid, tributyl naphthalene sulfonic acid, camphor sulfonic acid, and acrylamide-t-butyl sulfonic acid.

[0028]

Moreover, polyfunctional organic sulfonic acids with 2 or more sulfonic acid groups per molecule can be used in the present invention, and examples of such polyfunctional organic sulfonic acids are ethane disulfonic acid, propane disulfonic acid, butane disulfonic acid, pentane disulfonic acid, hexane disulfonic acid, heptane disulfonic acid, octane disulfonic acid, nonane disulfonic acid, decane disulfonic acid, benzene disulfonic acid, naphthalene disulfonic acid, toluene disulfonic acid, ethyl benzene disulfonic acid, propyl benzene disulfonic acid, butyl benzene disulfonic acid, dimethyl benzene disulfonic acid, diethyl benzene disulfonic acid, dipropyl benzene disulfonic acid, dibutyl benzene disulfonic acid, methyl naphthalene disulfonic acid, pentyl naphthalene disulfonic acid, hexyl naphthalene disulfonic acid, heptyl naphthalene disulfonic acid, octyl naphthalene disulfonic acid, nonyl naphthalene disulfonic acid, dimethyl naphthalene disulfonic acid, dipropyl naphthalene disulfonic acid, dibutyl naphthalene disulfonic acid, naphthalene trisulfonic acid, naphthalene tetrasulfonic acid, anthracene disulfonic acid, anthraquinone disulfonic acid, phenanthrene disulfonic acid, fluorenone disulfonic acid, carbazole disulfonic acid, diphenyl methane disulfonic acid, biphenyl disulfonic acid, terphenyl disulfonic acid, terphenyl trisulfonic acid, naphthalene sulfonic acid-formalin condensate, phenanthrene sulfonic acid-formalin condensate, anthracene sulfonic acid-formalin condensate, fluorene sulfonic acid-formalin condensate, and the carbazole sulfonic acid-formalin condensate, etc. The sulfonic acid group can be at any position in the aromatic ring.

[0029]

Furthermore, the organic acid can also be a polymer acid. Examples of such polymer

acids are polyvinyl sulfonic acid, polyvinyl sulfuric acid, polystyrene sulfonic acid, sulfonated styrene-butadiene copolymer, polyallyl sulfonic acid, polymethallyl sulfonic acid, poly-2-acrylamide-2-methyl propane sulfonic acid, poly halogenated acrylic acid, polyisoprene sulfonic acid, N-sulfo alkylated polyaniline, nuclear-sulfonated polyaniline, etc. Fluorine-containing polymers commonly known as Nafion (registered trademark of DuPont, U.S.) are also preferred polymer acids.

[0030]

The method whereby a basic substance such as triethyl amine is also added with the dopant, as explained in Japanese Kokai Patent No. Hei 3(1991)-28229, is also an ideal method for introducing dopants consisting of the aforementioned protic acid to the film-forming solution of this invention.

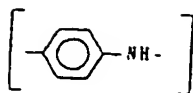
[0031]

This type of protic acid makes the polyaniline conductive by proton conversion of the quinone diimine structure to the imine nitrogen of the polyaniline represented by general formula (I). As previously mentioned, the m and n values in the formula for the quinone diimine/phenyl diamine-type polyaniline represented by aforementioned general formula (I) that is obtained in this way are approximately the same.

[0032-0034]

Thus, quinone diimine-phenylenediamine-type polyaniline has a high quinone diimine structure content and therefore, it provides polyaniline with very high conductivity when it is doped by a protic acid. By means of this invention, polyaniline that is solvent-soluble and has the imino-p-phenylene structure represented by the formula

[Chemical Formula 2]



as its main repeating structural unit (referred to below as imino-p-phenylene-type polyaniline) is even more soluble in a variety of solvents than the aforementioned quinone diimine-diphenyldiamine-type polyaniline and therefore, it can be used with the aforementioned quinone diimine-phenylene-diamine-type polyaniline, or it can be used in place of the aforementioned quinone diimine-phenylene-diamine-type polyaniline.

[0035]

This type of imino-p-phenylene-type polyaniline can be obtained by reduction of the aforementioned quinone diimine-phenylene-diamine-type polyaniline with a reducing agent, as described in Japanese Kokai Patent No. Hei 3(1991)-52929. It is preferred that this type of imino-p-phenylene-type polyaniline also have a limiting viscosity $[\eta]$ as determined at 30°C in N-methyl pyrrolidone of 0.40 dl/g or higher.

[0036]

Phenyl hydrazine, hydrazine, hydrazine hydrate, hydrazine sulfate, hydrazine chloride, and other hydrazine compounds, or reducing hydrogenated metal compounds, such as lithium aluminum hydride, lithium borohydride, etc., be used as the reducing agent. A residue does not form after the reduction reaction and therefore hydrazine hydrates or phenyl hydrazine are particularly preferred as the reducing agent.

[0037]

When this type of imino-p-phenylene-type polyaniline is used, a film-forming solution

containing this polyaniline is cast onto a substrate to form a layer of the aforementioned film-forming solution on the substrate, the product is heated to form a resin sheet on the substrate, then this resin sheet is peeled from the substrate and is further heated for imidation of the polyamide acid. Quinone diimine-phenylene diamine-type polyaniline is formed by air oxidation. When the film-forming solution contains dopant, this quinone diimine-phenylene diamine-type polyaniline is doped to form conductive polyaniline and obtain a semi-conductive resin sheet.

[0038]

There are no particular restrictions to the shape of the semi-conductive resin sheet of this invention and as previously described, flat or curved sheets as well as tubes can be made. Moreover, the sheets can be discontinuous or continuous.

[0039]

Results of the Invention

By means of this invention, as previously explained, a semi-conductive resin sheet made from polyimide and (un)doped polyaniline can be easily obtained by forming a film from a film-forming solution comprising polyimide and undoped polyaniline (and dopant that can dope this polyaniline to conductivity).

[0040]

The semiconductive resin sheet obtained from undoped polyaniline of this invention does not originally contain dopant and therefore, there is essentially no change in conductivity, even with changes in environmental conditions, such as humidity, etc. On the other hand, by means of this invention, when a film-forming solution comprising undoped polyaniline and dopant that can dope this polyaniline to conductivity is used to make a conductive resin sheet, a conductive

resin sheet is immediately obtained by forming a film, in contrast to the method whereby doping is performed after film production, and therefore, dopant is rarely lost from the sheet, regardless of the effects of the environment, such as moisture, heat, etc., and semi-conductivity that is stable with respect to the environment is obtained.

[0041]

Examples

Reference examples and examples of the method of this invention will be described.

However, this invention is not limited to these examples.

[0042]

Reference Example 1

Production of Doped Polyaniline by Oxidation Polymerization of Aniline

6000 g distilled water, 360 ml 36% hydrochloric acid, and 400 g aniline (4.295 mole) were introduced in this order to a separable flask with a capacity of 10 liters, to which a stirring device, thermometer and straight tube adapter were attached. in order to dissolve the aniline. At the same time, 434 g 97% concentrated sulfuric acid (4.295 moles) were added to 1493 g distilled water in a beaker while cooling over ice water and mixed to prepare an aqueous sulfuric acid solution. This sulfuric acid solution was then added to the aforementioned separable flask and the entire flask was cooled to -4°C in a low-temperature thermostatic tank.

[0043]

980 g ammonium peroxodisulfate (4.295 moles) were added to 2293 g distilled water in a beaker and dissolved to prepare an aqueous oxidizing agent solution. The entire flask was cooled in a low temperature thermostatic tank and then 1 ml per minute or less of the

aforementioned aqueous ammonium peroxydisulfate solution was added dropwise from the straight tube adapter to the aqueous acidic solution of the aniline salt using a tubing pump while keeping the temperature of the reaction mixture at -3°C or lower and stirring. The color of the initially colorless, transparent solution changed from greenish blue to dark green as polymerization proceeded and then a dark green powder precipitated. An increase in temperature was seen with precipitation of the powder from the reaction mixture, but the temperature inside the reaction system was kept at -3°C or lower. Moreover, once dropwise addition of the aqueous ammonium peroxodisulfate solution was completed, taking approximately 7 hours, stirring was continued for another hour at a temperature of -3°C or lower.

[0044]

The powder that was obtained was filtered and rinsed with water and then acetone and vacuum desiccated at room temperature to obtain 430 g conductive polyaniline doped with sulfuric acid in the form of a dark green powder.

Undoping of doped conductive polyaniline by ammonia

350 g of the aforementioned doped conductive polyaniline powder were added to 4 liters of 2N aqueous ammonia and stirred for 5 hours at 5000 rpm using an autohomomixer. The mixture turned from dark green to bluish violet. The powder was filtered with a Buchner funnel and the filtrate was repeatedly rinsed with distilled water until neutral while being stirred in a beaker. Then the filtrate was rinsed with acetone until it was colorless. The powder was vacuum desiccated for 10 hours at room temperature to obtain 280 g dark green undoped polyaniline powder.

[0045]

Reference Example 2

Preparation of polyimide precursor solution A

An almost equi molar mixture of 3,3',4,4'-biphenyl tetracarboxylic dianhydride and p-phenylene diamine was reacted for 12 hours at a temperature of 20 to 60°C in an N-methyl-2-pyrrolidone solution (concentration of 20 wt%) to obtain a polyamide acid solution with a viscosity of 1000 poise (as determined with a B-type viscometer at a temperature of 25°C) and an inherent viscosity of 2.1.

[0046]

Preparation of Polyimide Precursor Solution B

An almost equi molar mixture of pyromellitic dianhydride and 3,3',4,4'-diamino diphenyl ether was reacted for 10 hours at a temperature of 5 to 20°C in N-methyl-2-pyrrolidone solution (concentration of 20 wt%) to obtain a polyamide acid solution with a viscosity of 2000 poise (as determined with a B-type viscometer at a temperature of 25°C) and an inherent viscosity of 2.5.

[0047]

Example 1

2.98 g phenyl hydrazine were dissolved in 180 g N-methyl-2-pyrrolidone and then 20 g of the polyaniline powder obtained in Reference Example 1 was dissolved in this to obtain a 10 wt% undoped polyaniline solution. Next, 100 g of the polyimide precursor solution A obtained in Reference Example 2 was added to this polyaniline solution and stirred for 1 hour to obtain a

film-forming solution of undoped polyaniline and polyimide precursor.

[0048]

Using this film-forming solution, a film was made as follows. That is, after coating the aforementioned film-forming solution on a glass sheet using a knife coated with a gap of 120 μm the product was treated for 20 minutes at 150°C, 20 minutes at 200°C, 20 minutes at 250°C and finally, 20 minutes at 300°C, to remove the solvent and perform imidation. The product was peeled from the glass sheet to obtain a semicon-ductive resin sheet with a thickness of 15 μm made from a polymer blend of undoped polyaniline and polyimide.

[0049]

This conductive resin sheet was made from 50 wt% undoped polyaniline and 50 wt% polyimide, and it had a volume resistivity of $3 \times 10^{11} \Omega\text{cm}$, with the results of tensile testing a strength of 24 kgf/mm² and a modulus of 520 kgf/mm².

[0050]

Example 2

200 g of undoped polyaniline solution with a concentration of 10 wt% were prepared as in Example 1. Then, 300 g polyimide precursor solution B obtained in Reference Example 2 were added to this polyaniline solution and stirred for 1 hour to obtain a film-forming solution comprising undoped polyaniline and polyimide precursor.

[0051]

Using this film-forming solution, a film was made by the following method. That is, the aforementioned film-forming solution was coated on a glass sheet using a knife coater with a gap of 240 μm and then, as in Example 1, the solvent was removed and imidation was performed,

after which the film was peeled from the glass sheet to obtain a semiconductive resin sheet with a thickness of 30 μm comprising polyimide and undoped polyaniline polymer blend.

[0052]

This semiconductive resin sheet was made from 25 wt% undoped polyaniline and 75 wt% polyimide. Its volume resistivity was $4 \times 10^{12} \Omega\text{cm}$ and the results of tensile studies gave a strength of 16 kgf/mm² and a modulus of 260 kgf/mm².

[0053]

Example 3

200 g of an undoped polyaniline solution with a concentration of 10 wt% was prepared as in Example 1. At the same time, 12.6 g p-toluene sulfonic acid monohydrate (dopant) were dissolved in 113.5 g N-methyl-2-pyrrolidone to prepare a 10 wt% p-toluene sulfonic acid solution. Next, these two solutions were mixed to prepare the doped polyaniline solution.

[0054]

After adding 100 g polyimide precursor solution A obtained in Reference Example 2 to this solution, it was stirred for one hour to obtain a film-forming solution comprising doped polyaniline and polyimide precursor. This film-forming solution was coated on a glass sheet with a knife coater having a gap of 240 μm . Then, it was heated for 30 minutes at 150°C to remove the solvent. The sheet that was obtained in this way was peeled from the glass plate and heated for 20 minutes at 300°C to obtain a semiconductive resin sheet with a thickness of 25 μm made from a polymer blend of polyimide and polyaniline doped with p-toluene sulfonic acid.

[0055]

This semiconductive resin sheet was made from 50 wt% doped polyaniline and

50 wt% polyimide and had a thickness of 25 μm . When volume resistivity of this semiconductive resin sheet was determined, it was $8 \times 10^{10} \Omega\text{cm}$. Moreover, surface resistance was $2 \times 10^9 \Omega$. The aforementioned semiconductive sheet was immersed for 24 hours in distilled water. After drying, volume resistivity was determined to be $1 \times 10^{11} \Omega\text{cm}$.

[0056]

200 g 10 wt% undoped polyaniline solution were prepared as in Example 1. At the same time, 21.5 g dodecyl benzene sulfonic acid (dopant) were dissolved in 193.5 g N-methyl-2-pyrrolidone to prepare a 10 wt% dodecyl benzene sulfonic acid solution. Next, these two solutions were mixed together to obtain the doped polyaniline solution.

[0057]

After adding 100 g polyimide precursor solution A obtained in Reference Example 2 to this solution, it was stirred for one hour to obtain a film-forming solution of doped polyaniline and polyimide precursor. This film-forming solution was coated onto a glass sheet using a knife coater with a gap of 240 μm and then heated for 30 minutes at 150°C to eliminate the solvent. The sheet that was obtained was peeled from the glass sheet and heated at 300°C for 20 minutes to obtain a semiconductive resin sheet with a thickness of 25 μm of a polymer blend of polyimide and polyaniline doped with dodecyl benzene sulfonic acid.

[0058]

This semiconductive resin sheet was made from 50 wt% doped polyaniline and 50 wt% polyimide and had a thickness of 25 μm . Volume resistivity of this semiconductive

resin sheet was $2 \times 10^{11} \Omega\text{cm}$. Moreover, surface resistance was $2 \times 10^{10} \Omega$.

[0059]

Comparative Example 1

100 g p-toluene sulfonic acid were dissolved in 400 g distilled water and then 500 g methanol was added to this to prepare a dopant solution. A semiconductive resin sheet made from polyimide and undoped polyaniline polymer blend obtained in Example 1 was immersed in this dopant solution for 60 minutes in order to dope the polyaniline. Volume resistivity of the resin sheet that was obtained was $7 \times 10^{10} \Omega\text{cm}$. Moreover, when this resin sheet was immersed for 24 hours in distilled water as in Example 5 and dried, surface resistance was determined to be $9 \times 10^{11} \Omega\text{cm}$.

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